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Glycerol reforming in supercritical water; a short review

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ABSTRACT

Due to the rise in global biodiesel production, the amount of crude glycerol, the main byproduct, has increased steadily. Identification of high value added outlets for crude glycerol has been explored in detail to increase the overall economics of the biodiesel process. Examples are the use of glycerol for the synthesis of green biobased chemicals and the conversion to hydrogen and/or syngas. Supercritical water has received considerable attention as reaction medium for glycerol reforming because it allows the processing of streams with high moisture content and the production of clean gas at high pressure, being attractive from an environmental point of view. The recent interest in supercritical water reforming of biomass, especially glycerol, has created the need for the available data in this specific field to be collected and compared. This review, the first to deal exclusively with glycerol processing, focuses on the production of gas and of organic components in supercritical water. Both catalytic and non-catalytic reforming of glycerol is considered and thermodynamics are addressed. The results suggest that the process conditions during supercritical water reforming of glycerol should depend on the aimed products. Low temperatures, high pressures, concentrated feed solutions and acidic catalyst will generate liquid products, with acrolein as the main compound. For gasification, high temperatures, lower pressures, dilute feed solutions and alkali or metal catalysts should be used.

Contents

1. Introduction

The conversion of biomass to heat and power, biofuels and biobased chemicals has attracted a lot of attention recently, largely due to the environmental and socio-economic problems associated with the use of fossil fuels [1–3]. The main environmental concern refers to the generation of CO_2 during fossil fuel processing to produce energy and synthesize various chemicals. The production of biobased chemicals and energy carriers is considered to be carbon-neutral, since the CO_2 generated during processing can be absorbed by plants during their growth. One example is the conversion of biomass to green H_2, an excellent energy carrier that is expected to be an important next generation fuel [4,5].

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A very attractive platform chemical from biomass is glycerol, which was identified as a top 12 biobased chemical in recent studies by the department of energy of the US [6]. An overview of possible biobased chemicals derived from glycerol is given in Fig. 1. Glycerol is the main byproduct of the biodiesel industry and the global increase in the production of biodiesel (in 2010 European output of biodiesel was of 9.57 million tones [7]) has led to a simultaneous increase in the amount of crude glycerol, causing prices to drop. Therefore the identification of high value added outlets for crude glycerol, such as production of energy carriers (H_2, CH_4) or of other chemicals and chemical intermediates (acrolein, methanol, syngas) has become an active research topic and development area to increase the overall economics of the biodiesel process [8–10].

One of the possible conversion technologies for glycerol involves the use of supercritical water (SCW) as processing medium. SCW has received considerable attention recently and was shown a suitable reaction medium for biomass reforming. Supercritical water reforming (SCWR) of different types of biomass and of model compounds has been studied both with and without the addition of catalyst [11–17]. The presence of a catalyst is known to affect the rate of the conversion and the gas composition. As operating temperatures can be lowered when catalysts are used, the energy required for the process is lower and the operating costs of SCWR go down.

Despite the increasing interest in SCWR of glycerol, no review is available that would collect and compare the existing data. Therefore in this paper the authors provide a first overview of the relevant investigations on SCWR of glycerol. The review starts with a brief presentation of glycerol as byproduct from biodiesel production and of supercritical water reforming. Next the findings of different research groups on SCWR of glycerol are presented in two sections, as a function of the final reaction products, liquid compounds or gases. Finally a comparison of these findings is performed.

2. Materials

2.1. Glycerol

Glycerol is the main byproduct of a biodiesel production process involving the transesterification of triglycerides (Fig. 2). Approximately 1 kg of glycerol is produced for every 9 kg of biodiesel. Currently, glycerol is used in personal and oral care, food, tobacco, polymers and pharmaceutical applications and as co-feed for biogas production [18]. However, most of the glycerol byproduct from biodiesel plants is disposed without utilization, because of its impurities and the difficulties encountered during purification. These impurities include alkali metal catalysts, salts of fatty acids, excess methanol and fatty acid methyl esters [18].

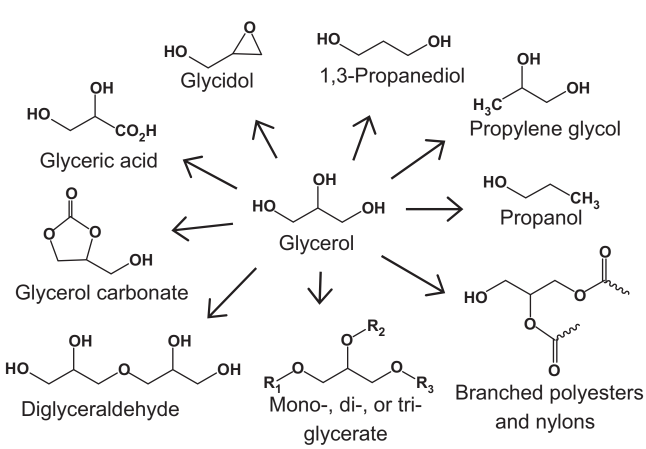


Fig. 1. Derivatives of glycerol [6].

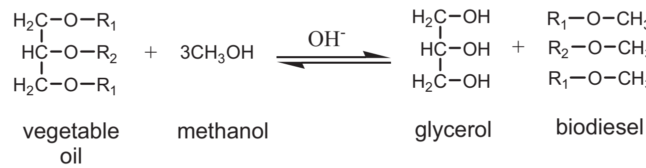


Fig. 2. The production of biodiesel and glycerol from vegetable oil.

Table 1
Relevant properties of water at different conditions [32].

	Water	Steam	Subcritical water	Supercritical water	
Temperature T (K)	298	673	523	673	673
Pressure P (MPa)	0.1	0.1	5.0	25.0	50.0
Density ρ (g/cm^3)	1	0.0003	0.80	0.17	0.58
Dielectric constant ε	78.5	~1	27.1	5.9	10.5
pK_w	14.0	/	11.2	19.4	11.9
Heat capacity c_p (kJ/kg/K)	4.22	2.1	4.86	13.0	6.8
Dynamic viscosity η (mPa s)	0.89	0.02	0.11	0.03	0.07
Heat conductivity λ (mW/m/K)	608	55	620	160	438

The global glycerol market, like other commodity markets, is known for its unpredictability and complex nature. In June 2000 the crude glycerol price stood above 800 US$/mt. Due to the production of large quantities of biodiesel and associated crude glycerol from 2000 onwards the price started to swing dramatically and after a free fall bottomed at a level below 100 US$/mt in June 2005. The crude glycerol price then recovered until the beginning of the economic recession, when demand and therefore market price fell rapidly again, to around 100 US$/mt in 2009. A further drop in the crude glycerol price was anticipated but did not materialize. Instead, in 2011 the glycerol price has been trending upwards due to European biodiesel production stabilizing and additional innovative glycerol applications, such as glycerol-derived propylene glycol and glycerol-derived epichlorohydrin, on the rise [19].

To increase the overall economics of the biodiesel process, several studies have been conducted on the conversion of glycerol to biobased chemicals (Fig. 1) and energy carriers such as H_2. Besides glycerol reforming in SCW, another hydrothermal process, steam reforming, has received high attention in the last years for syngas and H_2 production. In the latter process glycerol is catalytically converted to syngas and subsequently to H_2 at high temperature (600–1000 K) and atmospheric pressure in the presence of water. Typical catalysts used are: nickel [20–26], platinum [23,26–29], iridium [21,25], cobalt [21,26], copper [26], palladium and ruthenium [25], usually on CeO_2, Al_2O_3 or La_2O_3 supports.

2.2. Supercritical water

Water is in the supercritical state when both temperature and pressure are above the critical point (T_c=647 K, P_c=22.1 MPa). Relevant physico-chemical properties of water, such as density, dielectric constant, ion product, heat capacity and viscosity differ significantly from those in liquid water or water in the vapor phase (Table 1). At room temperature and atmospheric pressure the dielectric constant of water is high. As temperature and pressure increase, there is a sharp decline in the dielectric constant. This change affects the solubility of other components

in water and actually SCW behaves as a nonpolar solvent. As a consequence, the dissolving capacity for polar (inorganic) compounds decreases [11,30–32]. At elevated temperatures, the viscosity of water decreases, which results in higher values for diffusion coefficients of dissolved compounds. The density and ion product of SCW are also lower than those of water at normal conditions. This may result in changes in reaction mechanisms when modifying the reaction conditions from ambient to subcritical and supercritical conditions [11]. Therefore, depending on the conditions of temperature and pressure, either free radical or polar and ionic reactions may take place. Decomposition of biomass in sub- and supercritical water is fast, high solubility of the intermediates in SCW inhibits tar and coke formation and high product yields are obtained at relatively low temperatures [33,34].

SCW has been used as a processing medium for various types of biomass and model compounds such as cellulose [12,13], lignin [14,15], glucose [16,17] etc. Glycerol is a promising biomass feedstock for SCWR. Crude glycerol contains water and its hydrothermal conversion can be performed without prior drying. Besides water, methanol, fatty acid methyl esters and salts are also present in crude glycerol as impurities. In SCW the solubility of most ionic species is low and as a result salts that are present in the feedstock will tend to precipitate from the solution. They may precipitate on the reactor wall, in or on the pipes or on the catalyst surface, reducing its effective surface area and activity. Therefore salt removal is an important part of supercritical-water technologies [35,36].

During SCWR of glycerol with or without a catalyst low molecular weight liquid components and permanent gases can be obtained. The production of liquid components aims to the formation of chemical intermediates, mainly acrolein. Sulfuric acid or sulfates were used for the dehydration of glycerol [37–40]. However, these catalysts were difficult to recover from the reactor effluent. They may cause corrosion problems and may also plug the reactor as the solubility of salts in SCW is low. Alkali compounds, such as Na_2CO_3 [41] or NaOH [42] were also proposed as catalysts. The main concern of all groups studying glycerol reforming in SCW is to increase feed conversion and reaction selectivity. The main goal when obtaining permanent gases is the production of H_2, but in all cases a gas mixture is obtained. The gas mixture consists of H_2, CO, CO_2, methane and higher hydrocarbons. The composition strongly depends on the process conditions [43].

In Table 2 an extensive overview of catalysts, reaction conditions and reaction products for glycerol reforming is given. The experimental procedure and results of the studies reviewed in Table 2 are described in the following paragraphs.

3. Glycerol reforming in supercritical water

3.1. Obtaining low molecular weight liquid components

Glycerol was decomposed in SCW to obtain chemical intermediates, mainly acrolein, which could be further used in chemical syntheses. Glycerol conversion and acrolein selectivity were the main parameters studied by all.

Antal et al. [37] investigated cellulose and glycerol decomposition in SCW using $NaHSO_4$ as catalyst. The reaction products consisted of acrolein, acetaldehyde and a gaseous mixture containing mainly H_2 and CO_2. It was shown that the catalyst enhances acrolein formation at 633 K, but has practically no effect on the product yields at 773 K. The results indicate that at higher temperatures a free radical mechanism is dominant in glycerol decomposition, with carbon–carbon cleavages leading to the formation of gases, whereas at lower temperatures heterolytic reactions involving ionic intermediates lead to the formation of acrolein.

Ramayya et al. [38] studied the acid-catalyzed dehydration of ethanol, *n*-propanol, ethylene glycol and glycerol in SCW. They found that glycerol is relatively stable in water at 34.5 MPa and 573 K. By adding small amounts of sulfuric acid, the dehydration of glycerol to acrolein occurred between 573 K and 623 K. Acetaldehyde was formed as a byproduct of the reaction. The authors explained the catalytic behavior of sulfuric acid by the fact that at higher pressure and above 673 K mineral acids dissociate in water and catalyze a variety of heterolytic bond cleavages.

Krammer et al. [32] showed that hydration, dehydration and hydrolysis reactions take place in SCW without additional catalysts, such as acids or bases, with high selectivity and with high yields. For glycerol they observed that the reaction takes place at temperatures higher than 623 K, with the formation of acrolein and water.

Bühler et al. [44] analyzed the products obtained during the decomposition of glycerol in near- and supercritical water. For the reaction conditions employed (Table 2), they obtained a conversion up to 31%. Formation of gaseous products occurs at temperatures above 673 K, as products of free radical mechanism. The formation of gaseous products decreases with pressure. The main products of the glycerol degradation are: methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, CO, CO_2, and H_2. Minor products are: acetone, ethane, ethene, propene, propane, butenes, butanes, methyl-hydroxy-dioxanes and some other products with higher molar masses. Two reaction pathways were proposed, viz. (i) pathway in which ionic reactions prevail (higher pressures and/or lower temperatures) yielding acetaldehyde, formaldehyde and propionaldehyde, and (ii) free radical degradation (lower pressures and/or higher temperatures), mainly to methanol, allyl alcohol, CO, CO_2 and H_2. Acrolein is found in both pathways as a by-product.

Zinc sulfate was used as a catalyst by Ott et al. [39]. The maximum obtained acrolein selectivity was 75 mol% at 633 K, 25 MPa and a catalyst concentration of 470 ppm which corresponded to a glycerol conversion of 50%.

The dehydration of polyols in sub- and supercritical water was studied by Lehr et al. [40]. They used 1,2- and 1,3-propanediol, 1,2-butanediol, glycerol and *m*-erythritol. At 633 K and 34 MPa glycerol was converted into acrolein using $ZnSO_4$ as catalyst. The influence of the residence time on the reaction output was analyzed and a maximum conversion to acrolein was observed after approximately 90 s.

Watanabe et al. [45] conducted experiments for glycerol conversion in sub- and supercritical water using both batch and flow reactors with and without the addition of H_2SO_4. In the absence of acid catalyst glycerol conversion was lower in batch experiments than in continuous ones. The conversion increased with temperature and reaction time, while the yield of acrolein decreased with increasing conversion due to subsequent decomposition reactions. Addition of H_2SO_4 enhanced glycerol conversion and acrolein selectivity. The yield of acrolein also increased with increasing pressure and initial concentration of glycerol, and it decreased at higher residence times. The group also proposed a simple kinetic model for acrolein formation.

In a study by Qadariyah et al. [46] the degradation products of glycerol at limited temperatures < 673 K were mainly acetaldehyde, acrolein and allyl alcohol, and a high glycerol conversion was obtained (99.92%). Acetaldehyde was formed only in subcritical water; allyl alcohol was identified only in supercritical conditions while acrolein was formed both in sub-critical and supercritical conditions. The distribution of products was explained by a change in the reaction pathways, going from ionic to free radical reactions.

Table 2
Overview of reaction conditions and catalysts for glycerol reforming in supercritical water.

Catalyst	Reactor type	$C_{glycerol}$ (wt%)	Temperature (K)	Pressure (MPa)	Reaction time (s)	Products	Ref.
$NaHSO_4$	Not known	Not known	633,773	35	90	Acrolein, acetaldehyde, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6; up to 32% glycerol conversion	[37]
H_2SO_4	Flow reactor Hastelloy C276	5	573–623	34.5	16–39	Acrolein, acetaldehyde, CO_2, C_2H_4, CO; up to 32% glycerol conversion	[38]
–	Flow reactor Inconel 625	5	523–673	25	120	Acrolein	[32]
–	Flow reactor Inconel 625	Not known	622–748	25, 35, 45	32–165	Methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, CO, CO_2, H_2, ethanol, acetone, C_2H_6, C_2H_4, propene, propane, butenes, butanes, methyl-hydroxy-dioxanes; up to 31% glycerol conversion	[44]
$ZnSO_4$	Flow reactor SS[b] 1.4401	1	573–663	25–34	10–60	Acrolein; up to 80% glycerol conversion	[39]
$ZnSO_4$	Flow reactor SS[b]1.4401	0.5–10	633	34	10–180	Acrolein	[40]
H_2SO_4	Batch reactor SS[b]316	2.33	573–673	25–34.5	600–3600	Acrolein (up to 74.3 mol%), acetaldehyde, formaldehyde, hydroxyacetone, allyl alcohol; up to 90% glycerol conversion	[45]
	Flow reactor SS[b] 316	0.65–3.24			5–80		
–	Batch reactor SUS 304	6.89–16.86	473–673	30	1200–3600	Acetaldehyde, acrolein, allyl alcohol; up to 99.92% glycerol conversion	[46]
TiO_2 WO_3/TiO_2	Flow reactor	0.46	673	33	Not known	Acrolein, acetaldehyde, propionic acid, hydroxylacetone, lactic acid, allyl alcohol, propionaldehyde, acetone, acetic acid, acrylic acid	[47]
CSAC[a]	Flow reactor Inconel 625	18.72	873	34.5	44	H_2, CO, CO_2, CH_4, C_2H_6	[48]
CSAC[a]	Flow reactor Hastelloy C276	18.72	938	28	60	H_2 (up to 51 mol%), CO, CO_2 (up to 35 mol%), CH_4, C_2H_6; up to 100% glycerol conversion	[49]
–	Flow reactor Hastelloy C276	18.71	980–991	28	40	H_2 (up to 52 mol%), CO, CO_2 (up to 36 mol%), CH_4; up to 98% glycerol conversion	[50]
–	Flow reactor	1	573–773	15–25	450	H_2 (more than 60%), CH_4, CO_2, formaldehyde; up to 40% glycerol conversion	[51]
Ru/TiO_2	Batch reactor Quartz capillary	1–20	673–1073	5–45	60	H_2 (up to 15%), CO (up to 55%), CO_2, CH_4, C_{2+} hydrocarbons; up to 100% glycerol conversion	[52]
Ru/Al_2O_3	Flow reactor Inconel 600	5–40	973–1073	24.1	5	H_2 (up to 70 mol%), CO, CO_2, CH_4; more than 99% glycerol conversion	[53]
Na_2CO_3	Flow reactor Hastelloy C276	1	653–773	25	59–296	H_2 (up to 60 mol%), CO, CO_2, CH_4, C_{2+} hydrocarbons; up to 98% glycerol conversion	[41]
NaOH	Batch reactor Hastelloy C	42.3[d]	573–673	8.5–31	240–2040	H_2 (up to 90 vol%), CO, CO_2, C_1–C_2 hydrocarbons	[42]
Ru/ZrO_2	Flow reactor	5	783–823	35	2–10	acetaldehyde, acetic acid, hydroxyacetone, acrolein, H_2, CO, CO_2; up to 100% glycerol conversion	[54]
K_2CO_3	Flow reactor Inconel 600	10	873	25	5	H_2 (up to 55 mol%), CO (up to 32 mol%) CO_2, CH_4; up to 100% glycerol conversion	[55]
– /Crude[c]	Flow reactor Incoloy 825	5–20	733–923	25.5–27.0	6–173	H_2, CO, CO_2, C_1–C_3 hydrocarbons; up to 100% glycerol conversion	[43]
$Pt/CeZrO_2$ Ni/ZrO_2 $Ni/CaO–6Al_2O_3$ $NiCu/CeZrO_2$ CuZn	Flow reactor Incoloy 825	10	648–973	25.5–27.0	8–87	H_2, CO, CO_2, CH_4, C_2H_6, C_{2+}; up to 100% glycerol conversion	[56]
$Ni/CaO–6Al_2O_3$	Flow reactor Incoloy 825	3–10	984–998	24–27	30–35	H_2, CO, CO_2, C_xH_y; 95.0–99.9% glycerol conversion	[57]
–	Pilot plant	6.6–40	923	25.5–31.6	/	H_2 (up to 53 mol%), CO, CO_2, CH_4	[58]
NaOH Na_2CO_3 KOH K_2CO_3	Flow reactor Hastelloy C276	10–50	718–873	25	3.9–9	H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6; up to 100% carbon and hydrogen gasification	[59]
K_2CO_3	Batch reactor Inconel 718SS[b]316	5, 10 (pure glycerol) 3.5 (crude glycerol)	723–873	25	300–7200	H_2, CO_2, CH_4, C_2H_6, acetaldehyde, propionaldehyde, acrolein, methanol, 1-propanol, ethylene glycol, allyl alcohol, 1,2-propanediol	[60]
NaOH	Batch reactor SS[b]316	10–30	573–703	30	5–120	H_2, CO_2, CO, CH_4, acetaldehyde, formic acid, glycolic acid, propionic acid, formaldehyde, acetone, methanol; up to 57.5% glycerol conversion	[61]

[a] Coconut shell activated carbon.
[b] Stainless steel.
[c] The crude glycerol contained NaCl.
[d] Concentration of glycerol in biodiesel byproduct.

The authors performed kinetic analysis and described the overall reaction rate by pseudo-first-order kinetics which showed that below the critical temperature the reaction rate increases while, in supercritical regions, the reaction rate decreases with increasing reaction time.

Akizuki and Oshima [47] studied the dehydration of glycerol in supercritical water at 673 K and 33 MPa using TiO_2 and WO_3/TiO_2 catalysts. They found that all catalysts promoted glycerol conversion and the reaction rate increased with an increase in WO_3 content. The main products of the reaction were acrolein and acetaldehyde, and the yield of acrolein increased in the presence of WO_3. A reaction route and a process kinetic involving first and pseudo-first order reactions were also proposed. The group also noticed that in supercritical water the structure of TiO_2 changed from anatase to rutile, and the addition of WO_3 suppressed this change.

3.2. Obtaining permanent gases

Commonly H_2 is commercially produced from glycerol by catalytic steam reforming. Recent investigations focused on the possibility of avoiding the use of expensive catalysts by increasing the reaction pressure and operating above the critical point of water. Extensive research is employed in optimizing the glycerol conversion and syngas yield (CO and H_2), and minimizing production of hydrocarbons.

Xu et al. [48] studied the SCWR of glycerol over various types of carbon catalyst (spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut shell activated carbon). The effect of temperature, pressure, feed concentration, reaction time and type of catalyst on the reforming of glycerol were reported. The results suggest that temperatures above 873 K and pressures above 25 MPa are required to achieve high conversion for concentrated organic feeds. It was also shown that the available surface area of the carbon catalyst does not greatly influence its effectiveness as a catalyst. With and without a catalyst, glycerol can be completely gasified to a hydrogen-rich gas, with carbon catalyst affecting the gas composition.

Coconut shell activated carbon was used as catalyst by Antal and Xu [49,50]. The results showed that almost all glycerol in the feed can be converted, the reaction being catalyzed both by the reactor wall and by carbon catalyst. It is suggested that the catalytic conversion of polyols to H_2, CO_2 and CO involves the preferential cleavage of carbon–carbon bonds and that Pt-based catalysts may be preferred.

Kambayashi and Nishi [51] studied the decomposition of methanol, acetic acid, ethanol and glycerol without a catalyst. At 773 K and 25 MPa they obtained a conversion efficiency of glycerol of 40.3%, H_2 representing more than 60% of the final gas mixture.

Kersten et al. [52] investigated the reforming of glycerol, glucose and pinewood. The batch experiments were performed in quartz capillary reactors, this allowing the assessment of the catalytic influence of a metal reactor wall, by comparison with previous studies. Pressures in the range of 5–50 MPa do not affect the conversion and product yield and, in the absence of catalyst, complete conversion to the gas phase is possible only for diluted feedstock solutions. It was also noticed that by increasing the temperature above 923 K the carbon conversion is not significantly increased. Inconel 625 powder added to the capillary reactors to analyze the catalytic influence of the reactor wall showed higher carbon conversions and higher yield of gases. Na^+ cations appear to promote the water–gas shift reaction, which leads to more H_2 and less CO but does not necessarily increase the carbon conversion.

Ru/Al_2O_3 was studied by Byrd et al. [53] (see also Table 2) as catalyst for SCWR of glycerol. The group observed that under the employed conditions glycerol was completely decomposed to H_2, CO_2 and methane along with small amounts of CO. They observed that the yield of H_2 is favored by dilute feed concentrations, short residence time and high temperature. Byrd et al. recommend the best conditions for producing H_2 being $T > 898$ K and a molar ratio of water to glycerol of 9:1. Under these conditions methane production is minimized and carbon formation is thermodynamically inhibited.

The effect of Na_2CO_3 on SCWR of glycine and glycerol was shown by Xu et al. [41], demonstrating a lower glycerol conversion and lower H_2 yield.

Onwudili and Williams [42] studied crude glycerol (mainly glycerol, methanol and fatty acid methyl esters) in the presence of water under sub- and supercritical conditions. NaOH was used as catalyst, and the results were compared with those for pure glycerol. With increasing concentration of NaOH more H_2 was formed, while the concentrations of CO, CO_2 and hydrocarbons show decreasing trends. The group also observed that the formation of carbon can be suppressed in the presence of NaOH.

May et al. [54] conducted experiments for the conversion of glycerol in SCW with and without catalyst. In the absence of catalyst, at 35 MPa and 783 K the highest conversion of glycerol was of 22% and was obtained after 8.5 s. The main reaction products were acetaldehyde, hydroxyacetone and acetic acid. Gaseous products comprised H_2, carbon oxides and methane. At higher temperature (823 K) almost complete conversion was achieved after 8 s. Under these conditions the yields of liquid products reached a maximum and, at high glycerol conversion, started to decrease due to decomposition to gases, especially carbon oxides. The group observed that the use of 1 wt% Ru/ZrO_2 catalyst enhanced glycerol conversion significantly. Acetic acid became the main condensable product instead of acetaldehyde and the yields of H_2, carbon oxides and methane increased. However carbon production was noticed following catalyzed reactions, especially at lower temperature. It was concluded that although the Ru/ZrO_2 catalyst presented good stability and overall activity, its selectivity towards reforming reactions was not high enough in the studied temperature range.

Chakinala et al. [55] conducted glycerol reforming experiments in a continuous flow reactor for 10 wt% glycerol solution and in the presence of amino acids (L-alanine, glycine, and L-proline) and alkali salt (K_2CO_3). For solutions without additives the group obtained a glycerol conversion of 66% (at 873 K and 25 MPa) without char formation, while the gas products consisted of H_2, CO, CO_2, methane and small amounts of C_2–C_3 hydrocarbons. Glycerol conversion and gas yield were favored by increasing temperature and residence time. The gasification of glycerol was not affected by the presence of L-alanine and glycine. The presence of L-proline however caused a significant reduction of the gasification efficiency and gas yield. All amino acids induced the formation of char. The addition of K_2CO_3 lead to a complete conversion of glycerol and intensified the H_2 yield by promoting the water–gas shift reaction. The group also performed chemical equilibrium calculations based on Gibbs free energy minimization, using a modified Soave–Redlich–Kwong equation of state to calculate the fugacity coefficients.

Van Bennekom et al. [43] investigated the reforming of pure glycerol, crude glycerol and methanol in SCW. The experiments were performed both in a laboratory scale unit (1 L aqueous feed/h) and a pilot plant (10 L aqueous feed/h) at temperatures between 723 and 923 K and pressures between 25.5 MPa and 27 MPa. H_2, CO, CO_2, methane and higher hydrocarbons were produced with comparable efficiencies for both pure and crude glycerol. Conversion increased with temperature and residence

time for both types of glycerol. The presence of alkali (Na_2CO_3) in the feed enhanced glycerol conversion at low temperatures, while the effect was less visible at higher temperatures. The group noticed that the effect of the feed concentration on glycerol conversion and gas yield was more pronounced for the SCWR of crude glycerol, where the salt deposition may result in the loss of catalytic activity of the reactor wall. No coke formation was observed and only minor quantities of liquid products (propionic acid, acetaldehyde, acetic acid, formaldehyde, methanol, and ethanol) were detected in the effluent. The group also performed experiments to determine the extent and progress of the water–gas shift reaction as a function of the operating conditions. For these experiments pure gases were mixed with water, introduced in the reactor and the output gas mixture was analyzed. The results showed that the water–gas shift reaction has a minor effect on the overall process, with slightly higher activity in the presence of Na_2CO_3. The group also calculated equilibrium gas yields at complete conversion and compared the results with experimental data.

Van Bennekom et al. [56] also investigated a range of metallic catalysts, $Pt/CeZrO_2$, Ni/ZrO_2, $Ni/CaO–6Al_2O_3$, $NiCu/CeZrO_2$ and a CuZn alloy, for their influence on the carbon-to-gas efficiency and gas composition in the reforming of glycerol in SCW. The experimental conditions are summarized in Table 2. The results showed that the presence of catalysts improved the decomposition of glycerol into gaseous components. All catalysts promoted the water–gas shift reaction, while the ones based on Ni also promoted methanation. Coke was form when using Ni/ZrO_2 and $Pt/CeZrO_2$, which might be responsible for the reduction in activity at longer runtimes for these two catalysts. The group observed that the gas composition was significantly influenced by the presence and type of catalyst and they concluded that catalysts act upon glycerol decomposition in three stages: (i) initial decomposition of glycerol into water-soluble intermediate products; (ii) the conversion of these intermediate products to gas; and (iii) gas phase reactions. Equilibrium gas yields were also calculated and the results were compared to the experimental data.

Next the group integrated SCWR into a process for the synthesis of methanol from aqueous glycerol [57]. Glycerol reforming was carried out at pressures of 24–27 MPa and temperatures of 948–998 K with 3–10 wt% feed concentrations. Different approaches were followed to obtain an appropriate stoichiometric ratio of the syngas: external H_2 was added to the syngas after the reformer; a $Ni/CaO–6Al_2O_3$ catalyst was used to reduce the hydrocarbon content and to promote the water–gas shift reaction; and different feed concentrations were used. The glycerol conversion was almost complete for all experiments.

Based on results regarding the SCWR of glycerol into H_2 rich synthesis gas, Anger et al. [58] designed and built a pilot plant for which the required thermal energy would be supplied by a porous burner unit using glycerol and a part of the synthesis gas as fuel. The fuel gas resulting from the pilot plant consisted of H_2, methane, CO and CO_2, and its composition was dependent on the water/glycerol ratio in the feed. The H_2 yield increased with increasing water content, while CO and methane yields decreased. This fuel gas was used to operate an engine and to produce electrical and thermal energy.

Guo et al. [59] performed glycerol gasification by supercritical water in a continuous flow tubular reactor at 718–873 K and 25 MPa, with short residence times of 3.9–9.0 s. Different alkali catalysts were used: NaOH, Na_2CO_3, KOH and K_2CO_3. The effect of reaction temperature, residence time, glycerol concentration and type of catalyst on gasification was studied. The results showed that the gasification efficiency was favored by higher temperatures, long residence times and lower glycerol concentration. The alkali catalysts enhanced the water–gas shift reaction, NaOH being the most active. No char was observed in all experiments. The group also performed a simple kinetic study by assuming pseudo first order kinetics.

Yu-Wu et al. [60] reported about the supercritical water conversion, with and without catalyst (K_2CO_3), of crude glycerol compared to pure glycerol. The group used batch reactors to analyze the formation of intermediate compounds during glycerol decomposition. They observed that SCW gasification of crude glycerol favored the formation of light hydrocarbons, while pure glycerol promoted H_2 production. The difference between the two feeds was explained by the presence of sodium salts in crude glycerol. The gasification efficiency increased with process temperature, reaction time and the use of catalyst. Acrolein was mainly produced in the absence of catalyst, and no char was formed during the reactions.

Müller and Vogel [61] studied coke formation during hydrothermal reforming of glycerol. They developed a procedure for separating and measuring the amounts of both tar and coke formed during the reaction. The batch experiments were conducted in a temperature range of 573–703 K, residence times of 5–120 min and feed concentrations up to 30 wt% at pressures around 30 MPa. Coke formation was observed at subcritical temperatures and long residence times, and the amount of coke decreased at higher temperatures and diluted feed solutions. NaOH, added to change the pH of the reaction mixture, seemed to inhibit the conversion of glycerol [61].

3.3. Thermodynamic analysis

The experimental results presented by the various groups on glycerol reforming in SCW have shown that a wide range of products and compositions is attainable by varying the process parameters such as temperature, pressure, feed ratio, reaction time or type of catalyst. To optimize the yields of useful products, such as H_2 or acrolein, it is necessary to apply thermodynamic models which can accurately predict the outcome of a reaction under certain conditions when at equilibrium and therefore set the yield boundaries.

Thermodynamics of glycerol reforming in SCW were studied by several researchers [62–69]. Voll et al. [62] used Gibbs free energy minimization and gas fugacities to calculate the equilibrium composition for SCW gasification of methanol, ethanol, glycerol, glucose and cellulose. For glycerol, the equilibrium gas yield was calculated as a function of temperature, at a pressure of 24.1 MPa and feed concentration of 5 wt%. The results were compared with the experimental data obtained by Byrd et al. [53]. Based on both theoretical and experimental data the group concluded that low feed concentrations of glycerol and high temperatures lead to higher H_2 yields.

In the work by Castello and Fiori [63] SCWR of glycerol was analyzed by means of a two-phase non-stoichiometric thermodynamic model, based on Gibbs free energy minimization. Two different types of analysis were performed: the first addressing the conditions that lead to the formation of char, and the second focused on energy aspects. The analysis indicated that the formation of char is favored at high feed concentration (higher than 60 wt%), higher pressure (over 1 MPa) and lower temperature (less than 1173 K). The simulations performed to evaluate the energy needs of SCWR showed that the process is weakly exothermic for temperatures below 953 K and weakly endothermic above 953 K. The model results were compared with the experimental data obtained by Byrd et al. [53] and a very good agreement was obtained for the H_2 yield.

Gutiérrez Ortiz et al. [64,65] performed a systematic thermodynamic analysis by the total Gibbs free energy minimization method (AspenPlus^{TM} software using Soave–Redlich–Kwong equation of state

(EOS) for the simulation of the supercritical region). The analysis has been conducted on SCWR of pure and crude glycerol, with [64] and without partial oxidation [65]. The aim was to identify the operating conditions that maximize H_2 production. It was found that crude glycerol generates less H_2 than pure glycerol, due to the presence of methanol (20 wt%). The analysis also showed that feed composition influences the resulting gas; if the water/glycerol ratio decreases, H_2 and CO yields decrease, while methane yield increases. Therefore high water concentration benefit high H_2 yield. Based on these results Gutiérrez Ortiz et al. [66] proposed an energy self-sufficient system for reforming glycerol with supercritical water by using the product gas as fuel to provide the thermal energy required by the reforming process. Using AspenPlus^{TM} software, the group investigated the effect of the main operating parameters on power production and analyzed the overall thermodynamic efficiency. The system was further integrated in a methanol synthesis process [67]. The gases obtained from glycerol reforming were expanded in a turbine, next upgraded by pressure swing adsorption technology and then fed into a methanol synthesis loop. Part of the unreacted synthesis gas was recycled while a fraction of it was purged. The energy required in the process was provided by burning some of the produced gasses. Some parameters (temperature, water-to-glycerol mass ratio and purge ratio) were analyzed for optimizing the overall process relative to methanol and power production. The group concluded that the highest yield of methanol (0.270 kg MeOH/kg glycerol) and overall energy efficiency (38.0%) are obtained by glycerol reforming at 1273 K and 24 MPa, using a water-to-glycerol mass ratio of 1.68 and a purge ratio of 0.2 [59].

Fiori et al. [68] analyzed the supercritical water gasification of glycerol, microalgae, sewage sludge, grape marc and phenol for H_2 production in terms of process development and energetic self-sustainability. They proposed a plant design simulated by means of AspenPlus^{TM} software and they studied the possibility of sustaining the reaction by burning the resulting gas mixture, while purified H_2 is fed to fuel cells. Simulations were performed at various operating conditions: different temperatures (773 K, 973 K and 1173 K), pressures (25.0, 30.0 and 35.0 MPa) and feed concentrations ranging from 5 wt% to 35 wt%. The results showed that syngas and methane production rises as the glycerol feed concentration increases, while H_2 production first increases, then stabilizes around a maximum, and finally starts to decrease. An increase in the temperature causes a significant rise in the H_2 production. The reaction can be energetically sustained by burning the produced syngas if a minimum glycerol feed concentration of 15–25 wt% is used, since at this concentration the H_2 production is maximal [68].

Azadi [69] proposed an integrated reforming process for the production of hydrogen and methane from wet biomass, using glycerol as model compound. Ru and Ni were considered as appropriate catalysts for the reforming of glycerol and water–gas shift reaction, while the required energy was provided by molten salts previously heated by solar energy. For the process, simulated by AspenPlus^{TM} software and Peng–Robinson equation of state, feed concentrations of 5, 10 wt% and 20 wt% were considered for gasification at 673–773 K and 25 MPa. The results show that the product gas consisted of methane, hydrogen and carbon dioxide, and that low temperatures and high feed concentrations favor higher methane yields. Azadi also analyzed the thermal and electrical efficiency of the integrated reforming/solar thermal system and compared it with that of the solar thermal/steam turbine system and the self-sufficient reforming process where the process heat is provided by combusting a fraction of the gas products. He concluded that the proposed integrated process eliminates the shortcomings associated with energy from fossil fuels and utilizes the solar energy stored in molten salts in a more efficient way compared to power generation by steam turbines.

4. Conclusions

This paper reviews the recent research on supercritical water reforming of glycerol which was studied by different groups as a promising technique for converting glycerol to useful products. In most studies the experiments were performed in flow reactors and the products consisted mainly of acrolein and acetaldehyde as liquid compounds and a gaseous mixture containing mainly H_2, CO_2 and CO (Table 2). The results show that the conversion of glycerol in supercritical water increases with temperature and reaction time [43,45,53,55,59–61], and is higher for dilute feed solutions [52,53,59]. The composition of the reaction output can be steered with the process conditions and the use of catalysts. ;It was suggested that at higher temperatures a free radical mechanism is dominant in glycerol decomposition, with carbon–carbon cleavages leading to the formation of gases, whereas at lower temperatures heterolytic reactions involving ionic intermediates lead to the formation of acrolein and other liquid compounds [37,44,46,60]. The formation of gaseous products decreases with increasing pressure [44] while the yield of acrolein increases with increasing pressure and initial concentration of glycerol, and decreases at higher residence times [45]. Also the yield of acrolein decreases with increasing conversion due to subsequent decomposition reactions [45]. The yield of H_2 is favored by dilute feed solutions, short residence time and high temperature [53,68].

Different catalysts have been proposed, and their influence has been analyzed and discussed. Metal salts, acids and alkalis were used as homogeneous catalysts. Metal salts ($NaHSO_4$, $ZnSO_4$) and acids (H_2SO_4) enhanced glycerol conversion and acrolein formation [37–40,45]. Since crude glycerol obtained from biodiesel industry always contains some alkalis due to base catalytic transesterification processes, the effect of alkali catalyst on SCWR of glycerol was also studied [41,42,55,59,60]. The results showed that the addition of alkali catalysts significantly increases the H_2 and CO_2 yields and decreases CO yield by promoting the water–gas shift reaction [52,59,60]. The main problem when using homogeneous catalysis is the low solubility of salts and alkalis in supercritical water, which may lead to precipitation and plugging of the reactor [59]. As heterogeneous catalysts, metals on different supports (Ru/TiO_2, Ru/Al_2O_3, Ru/ZrO_2, $Pt/CeZrO_2$, Ni/ZrO_2, $Ni/CaO–6Al_2O_3$, $NiCu/CeZrO_2$, CuZn) were used to increase glycerol conversion and the yield of gas formation [52–54,56,57]. Ruthenium and nickel catalysts promote methanation [56] while all metallic catalysts influence the water–gas shift reaction [56]. Coconut shell activated carbon was also proposed for enhancing glycerol gasification in supercritical water [48,49]. Because most tests were performed in metal reactors, the catalytic behavior of the reactor wall had to be also considered. It was found that the wall of the reactor favors glycerol conversion [49,50,52].

One of the biggest challenges associated with supercritical water reforming of glycerol is the formation and deposition of carbon, which may cause plugging of the reactor or deactivation of the catalyst. The results obtained by different groups showed that carbon formation may be suppressed by the application of high temperature [53,61], short residence time [61], low feed concentration [61] and the use of catalyst [42,43].

The experimental results were used for kinetic studies and for optimization of the process by thermodynamic analysis. The overall reaction rate was described by pseudo-first-order kinetics [46,47,59]. Gibbs free energy minimization was used to calculate the equilibrium composition for SCW gasification of glycerol [55,62–65]. In agreement with the experimental results, the thermodynamic studies showed that low feed concentrations of glycerol and high temperatures lead to higher H_2 yields [62,64,65] and char formation is favored at high feed concentration, higher pressure and lower temperature [61,63].

The results reviewed in this paper suggest that the conditions employed during supercritical water reforming of glycerol should depend on the target reaction products. Low temperatures, high pressures, concentrated feed solutions and acidic catalysts will generate liquid products, with acrolein as the main compound. For gasification, high temperatures, lower pressures, dilute feed solutions and alkali or metal catalysts should be used.

This review summarizes the experimental findings in a field with a high potential for industrial application. Despite the promising results obtained by various groups, we conclude that additional studies are still necessary for process optimization and scale-up.

References

[1] Rosillo-Calle F, De Groot P, Hemstock S, Woods J. The biomass assessment handbook: bioenergy for a sustainable environment. London: Earthscan; 2007.
[2] McGowan TF, Brown ML, Bulpitt WS, Walsh Jr. JL. Biomass and alternate fuel systems: an engineering and economic guide. New Jersey: John Wiley & Sons; 2009.
[3] Venkitasamy C, Hendry D, Wilkinson N, Fernando L, Jacoby WA. Investigation of thermochemical conversion of biomass in supercritical water using a batch reactor. Fuel 2011;90:2662–70.
[4] Rand DAJ, Dell RM. Hydrogen energy: challenges and prospects. Cambrdige: RSC Publishing; 2008.
[5] Ekins P. Hydrogen energy: economic and social challenges. London: Earthscan; 2010.
[6] Werpy T, Petersen G. Added Top Value Chemicals from biomass. vol. I—Results of screening for potential candidates from sugars and synthesis Gas. U.S.: Department of Energy; 2004.
[7] European Biodiesel Board. 2010–2011: EU biodiesel industry production forecasts show first decrease in 2011 since data is gathered; 2011.
[8] Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: a critical review. Renewable & Sustainable Energy Reviews 2010;14:987–1000.
[9] De Souza ACC, Silveira JL. Hydrogen production utilizing glycerol from renewable feedstocks—the case of Brazil. Renewable & Sustainable Energy Reviews 2011;15:1835–50.
[10] Ayoub M, Abdullah AZ. Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. Renewable & Sustainable Energy Reviews 2012;16:2671–86.
[11] Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY. Review of catalytic supercritical water gasification for hydrogen production from biomass. Renewable & Sustainable Energy Reviews 2010;14:334–43.
[12] Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T. Cellulose hydrolysis in subcritical and supercritical water. Journal of Supercritical Fluids 1998;13:261–8.
[13] Hao X, Guo L, Zhang X, Guan Y. Hydrogen production from catalytic gasification of cellulose in supercritical water. Chemical Engineering Journal 2005;110:57–65.
[14] Wahyudiono M, Sasaki MG. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water,. Chemical Engineering and Processing: Process Intensification 2008;47:1609–19.
[15] Furusawa T, Sato T, Sugito H, Miura Y, Ishiyama Y, Sato M. Hydrogen production from the gasification of lignin with nickel catalysts in supercritical water. International Journal of Hydrogen Energy 2007;32:699–704.
[16] Hao XH, Guo LJ, Mao X, Zhang XM, Chen XJ. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. International Journal of Hydrogen Energy 2003;28:55–64.
[17] Zhang L, Champagne P, Xu C. Screening of supported transition metal catalysts for hydrogen production from glucose via catalytic supercritical water gasification. International Journal of Hydrogen Energy 2011;36:9591–601.
[18] Pagliaro M, Rossi M. Future of glycerol. Cambridge: RSC Publishing; 2010.
[19] Chemical prices and chemical industry trends from ICIS pricing, 〈http://www.icispricing.com〉.
[20] Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, Chen H. Hydrogen production by sorption-enhanced steam reforming of glycerol. Bioresource Technology 2009;100:3540–7.
[21] Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. International Journal of Hydrogen Energy 2007;32:2367–73.
[22] Dou B, Rickett GL, Dupont V, Williams PT, Chen H, Ding Y, et al. Steam reforming of crude glycerol with in situ CO_2 sorption. Bioresource Technology 2010;101:2436–42.
[23] Iriondo A, Barrio VL, Cambra JF, Arias PL, Güemez MB, Navarro RM, et al. Influence of La_2O_3 modified support and Ni and Pt active phases on glycerol steam reforming to produce hydrogen. Catalysis Communications 2009;10:1275–8.
[24] Buffoni IN, Pompeo F, Santori GF, Nichio NN. Nickel catalysts applied in steam reforming of glycerol for hydrogen production. Catalysis Communications 2009;10:1656–60.
[25] Profeti LPR, Ticianelli EA, Assaf EM. Production of hydrogen via steam reforming of biofuels on $Ni/CeO_2–Al_2O_3$ catalysts promoted by noble metals. International Journal of Hydrogen Energy 2009;34:5049–60.
[26] Wen G, Xu Y, Ma H, Xu Z, Tian Z. Production of hydrogen by aqueous-phase reforming of glycerol. International Journal of Hydrogen Energy 2008;33:6657–66.
[27] Cui Y, Galvita V, Rihko-Struckmann L, Lorenz H, Sundmacher K. Steam reforming of glycerol: the experimental activity of $La_{1-x}Ce_xNiO_3$ catalyst in comparison to the thermodynamic reaction equilibrium. Applied Catalysis B: Environmental 2009;90:29–37.
[28] Slinn M, Kendall K, Mallon C, Andrews J. Steam reforming of biodiesel by-product to make renewable hydrogen. Bioresource Technology 2008;99:5851–8.
[29] Luo N, Fu X, Cao F, Xiao T, Edwards PP. Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst—effect of catalyst composition and reaction conditions. Fuel 2008;87:3483–9.
[30] Kritzer P. Corrosion in high-temperature and supercritical water and aqueous solutions: a review. Journal of Supercritical Fluids 2004;29:1–29.
[31] Marrone PA, Hong GT. Corrosion control methods in supercritical water oxidation and gasification processes. Journal of Supercritical Fluids 2009;51:83–103.
[32] Krammer P, Mittelstädt S, Vogel H. Investigating the synthesis potential in supercritical water. Chemical Engineering and Technology 1999;22:126–30.
[33] Kruse A. Hydrothermal biomass gasification. Journal of Supercritical Fluids 2009;47:391–9.
[34] Kruse A, Dinjus E. Hot compressed water as reaction medium and reactant: properties and synthesis reactions. Journal of Supercritical Fluids 2007;39:362–80.
[35] Peterson AA, Vontobel P, Vogel F, Tester JW. In situ visualization of the performance of a supercritical-water salt separator using neutron radiography. Journal of Supercritical Fluids 2008;43:490–9.
[36] Marrone PA, Hodes M, Smith KA, Tester JW. Salt precipitation and scale control in supercritical water oxidation-Part B: Commercial/full-scale applications. Journal of Supercritical Fluids 2004;29:289–312.
[37] Antal Jr. MJ, Mok WSL, Roy JC, Raissi AT, Anderson DGM. Pyrolytic sources of hydrocarbons from biomass. Journal of Analytical and Applied Pyrolysis 1985;8:291–303.
[38] Ramayya S, Brittain A, DeAlmeida C, Mok W, Antal Jr. MJ. Acid-catalysed dehydration of alcohols in supercritical water. Fuel 1987;66:1364–71.
[39] Ott L, Bicker M, Vogel H. Catalytic dehydration of glycerol in sub- and supercritical water: a new chemical process for acrolein production. Green Chemistry 2006;8:214–20.
[40] Lehr V, Sarlea M, Ott L, Vogel H. Catalytic dehydration of biomass-derived polyols in sub- and supercritical water. Catalysis Today 2007;121:121–9.
[41] Xu D, Wang S, Hu X, Chen C, Zhang Q, Gong Y. Catalytic gasification of glycine and glycerol in supercritical water. International Journal of Hydrogen Energy 2009;34:5357–64.
[42] Onwudili JA, Williams PT. Hydrothermal reforming of bio-diesel plant waste: products distribution and characterization. Fuel 2010;89:501–9.
[43] van Bennekom JG, Venderbosch RH, Assink D, Heeres HJ. Reforming of methanol and glycerol in supercritical water. Journal of Supercritical Fluids 2011;58:99–113.
[44] Bühler W, Dinjus E, Ederer HJ, Kruse A, Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. Journal of Supercritical Fluids 2002;22:37–53.
[45] Watanabe M, Iida T, Aizawa Y, Aida TM, Inomata H. Acrolein synthesis from glycerol in hot-compressed water. Bioresource Technology 2007;98:1285–90.
[46] Qadariyah L, Mahfud, Sumarno, Machmudah S, Wahyudiono, Sasaki M, et al. Degradation of glycerol using hydrothermal process. Bioresource Technology 2011;102:9267–71.
[47] Akizuki M, Oshima Y. Kinetics of glycerol dehydration with WO_3/TiO_2 in supercritical water. Industrial and Engineering Chemistry Research 2012;51:12253–7.
[48] Xu XD, Matsumura Y, Stenberg J, Antal Jr. MJ. Carbon-catalyzed gasification of organic feedstocks in supercritical water. Industrial and Engineering Chemistry Research 1996;35:2522–30.
[49] Antal Jr. MJ, Xu, X. Hydrogen production from high moisture content biomass in supercritical water. In: Proceedings of the U.S. DOE hydrogen program review, Alexandria, VA; April 1998.
[50] Antal Jr. MJ, Allen SG, Schulman D, Xu X, Divilio RJ. Biomass gasification in supercritical water. Industrial and Engineering Chemistry Research 2000;39:4040–53.
[51] Kambayashi, K, Nishi, Y. Possibility of hydrogen generation using supercritical water. In: Proceedings of EwDesign2003: third international symposium on environmentally conscious design and inverse manufacturing, Tokyo, Japan; December 2003.
[52] Kersten SRA, Potic B, Prins W, Van Swaaij WPM. Gasification of model compounds and wood in hot compressed water. Industrial and Engineering Chemistry Research 2006;45:4169–77.
[53] Byrd AJ, Pant KK, Gupta RB. Hydrogen production from glycerol by reforming in supercritical water over Ru/Al_2O_3 catalyst. Fuel 2008;87:2956–60.
[54] May A, Salvado J, Torras C, Montane D. Catalytic gasification of glycerol in supercritical water. Chemical Engineering Journal 2010;160:751–9.

[55] Chakinala AG, Brilman DWF, van Swaaij WPM, Kersten SRA. Catalytic and non-catalytic supercritical water gasification of microalgae and glycerol. Industrial and Engineering Chemistry Research 2010;49:1113–22.
[56] van Bennekom JG, Kirillov VA, Amosov YI, Krieger T, Venderbosch RH, Assink D, et al. Explorative catalyst screening studies on reforming of glycerol in supercritical water. Journal of Supercritical Fluids 2012;70:171–81.
[57] van Bennekom JG, Venderbosch RH, Assink D, Lemmens KPJ, Heeres HJ. Bench scale demonstration of the Supermethanol concept: the synthesis of methanol from glycerol derived syngas. Chemical Engineering Journal 2012;207: 245–53.
[58] Anger S, Trimis D, Stelzner B, Makhynya Y, Peil S. Development of a porous burner unit for glycerine utilization from biodiesel production by supercritical water reforming. International Journal of Hydrogen Energy 2011;36:7877–83.
[59] Guo S, Guo L, Cao C, Yin J, Lu Y, Zhang X. Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor. International Journal of Hydrogen Energy 2012;37:5559–68.
[60] Yu-Wu QM, Weiss-Hortala E, Barna R, Boucard H, Bulza S. Glycerol and bioglycerol conversion in supercritical water for hydrogen production. Environmental Technology 2012;33:2245–55.
[61] Müller JB, Vogel F. Tar and coke formation during hydrothermal processing of glycerol and glucose. Influence of temperature, residence time and feed concentration. Journal of Supercritical Fluids 2012;70:126–36.
[62] Voll FAP, Rossi CCRS, Silva C, Guirardello R, Souza ROMA, Cabral VF, et al. Thermodynamic analysis of supercritical water gasification of methanol, ethanol, glycerol, glucose and cellulose. International Journal of Hydrogen Energy 2009;34:9737–44.
[63] Castello D, Fiori L. Supercritical water gasification of biomass: thermodynamic constraints. Bioresource Technology 2011;102:7574–82.
[64] Gutiérrez Ortiz FJ, Ollero P, Serrera A. Thermodynamic analysis of the autothermal reforming of glycerol using supercritical water. International Journal of Hydrogen Energy 2011;36:12186–99.
[65] Gutiérrez Ortiz FJ, Ollero P, Serrera A, Sanz A. Thermodynamic study of the supercritical water reforming of glycerol. International Journal of Hydrogen Energy 2011;36:8994–9013.
[66] Gutiérrez Ortiz FJ, Ollero P, Serrera A, Galera S. An energy and energy analysis of the supercritical water reforming of glycerol for power production. International Journal of Hydrogen Energy 2012;37:209–26.
[67] Gutiérrez Ortiz FJ, Serrera A, Galera S, Ollero P. Methanol synthesis from syngas obtained by supercritical water reforming of glycerol. Fuel 2013;105: 739–51.
[68] Fiori L, Valbusa M, Castello D. Supercritical water gasification of biomass for H_2 production: process design. Bioresource Technology 2012;121:139–47.
[69] Azadi P. An integrated approach for the production of hydrogen and methane by catalytic hydrothermal glycerol reforming coupled with parabolic trough solar thermal collectors. International Journal of Hydrogen Energy 2012;37: 17691–700.